



TITLE:

Studies on Synthetic Pyrethroid. (XI) : Another Evidence for the trans- Configuration of a,o-Dimethylsorbic Acid

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ABSTRACTS

Studies on Synthetic Pyrethroid. (XI)

Another Evidence for the *trans*-Configuration of α,δ -Dimethylsorbic Acid

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Methyl α,δ -dimethylsorbate (I) gave methyl γ,δ -epoxy- α,δ -dimethyl- $\Delta\alpha$ -hexenoate (II), bp. 91-2°/6 mm., n_D^{20} 1.4672, by the epoxydation with perbenzoic acid. II was easily effected by treatment with dil. sulphuric acid and gave γ,δ -dihydroxy- $\alpha\delta$ -dimethyl- $\Delta\alpha$ -hexenoate (III), mp. 50-1°. Lead tetracetate cleaved the glycolic carbon-carbon linkage of III and gave β -monomethyl mesaconaldehyde (IV), bp. 76-8°/12mm., n_D^{20} 1.4680. 3,4-Dinitrophenylhydrazone of IV, mp. 204-4.5° IV was then oxidized with peracetic acid to β -monomethyl mesaconate (V), mp. 82-3°, diamide, mp. 117°; these were completely consistent with the literature. Cold saponification of V gave mesaconic acid (VI) mp. 202-3°, not depressed by the mixed mp. comparison with an authentic specimen. Di-*p*-phenylphenacyl ester of VI, mp. 204-5°.

Since the oxidation sequence involves no process likely to invert the geometrical configuration of double bond, the retention of the configuration in the parent compound can reasonably be concluded. Thus, the final formation of mesaconic acid of the well-established *trans*-configuration unambiguously shows the *trans*-configuration of the α,β -double bond of the parent methyl α,δ -dimethylsorbate (I).

Direct peroxidation of α,δ -dimethylsorbic acid also gave mesaconic acid in an inferior yield.

Resolution of (\pm) -*trans*-3-(*trans*-2'-Carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic Acid

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The partial resolution of (\pm) -*trans*-3-(*trans*-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid by means of a synthetic optical active $(-)$ - α -phenylethylamine to give the dextrorotatory acid, which was completely identical with the naturally derived acid, has already been described by the authors, and here, the complete resolution was achieved by obtaining the enantiomorphic laevorotatory acid with the results summarized below (rotations in ethanol).

	m.p.	$[\alpha]_D^{11}$
(+)-acid	163-4°	+70.9°
(\pm)-acid	206-8°	0
(-)-acid	163-4°	-70.5°